JÜLICH FORSCHUNGSZENTRUM

MAX DRIVING THE EXASCALE TRANSITION

Picking flowers: Hands-on FLEUR

Density Functional Theory and Electronic Structure Methods

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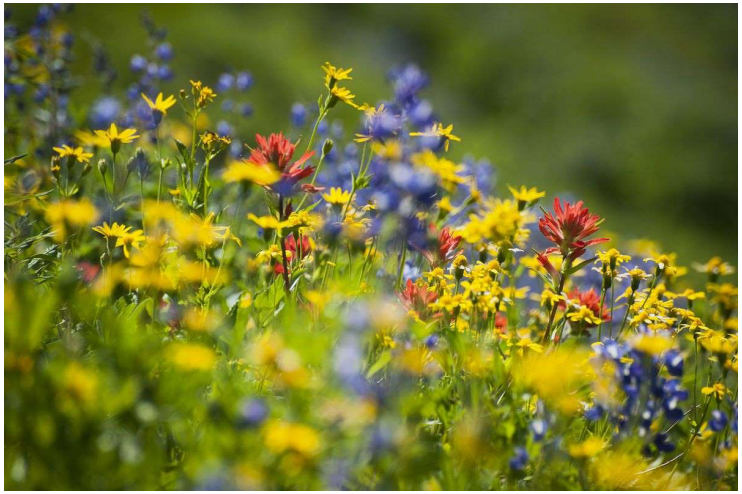
To pick, or not to pick…

COUNTRY LIVING

10 laws of picking wild flowers which, if broken, could land you a £5,000 fine



From daffodils to bluebells, it can often be tempting to pick them, but Brits could face a hefty fine or even imprisonment if they are picked from forbidden areas this spring, so it's important to know the rules...

When it comes to picking flowers, the law falls under two categories:

- *Wildlife and Countryside Act* of 1981
- *Theft Act* of 1968

Outline

- Get to know the laws and the restrictions they impose

How do we „calculate a material“?

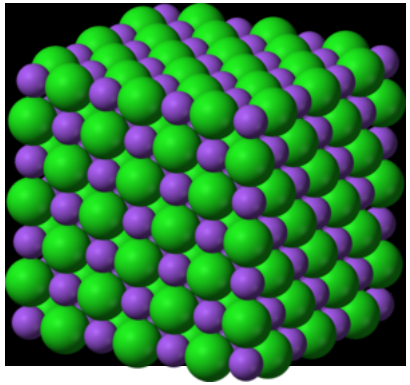
NaCl (table salt)

→ **Calculate the properties (e.g. lattice parameter, bulk modulus, phonons, electronic bands, magnetic properties etc.) from first principles**

WIKIPEDIA
The Free Encyclopedia

„In physics and other sciences, theoretical work is said to be **from first principles, or *ab-initio***, if it starts directly at the level of established science and **does not make assumptions such as empirical model and parameter fitting**.“

How do we „calculate a material“?



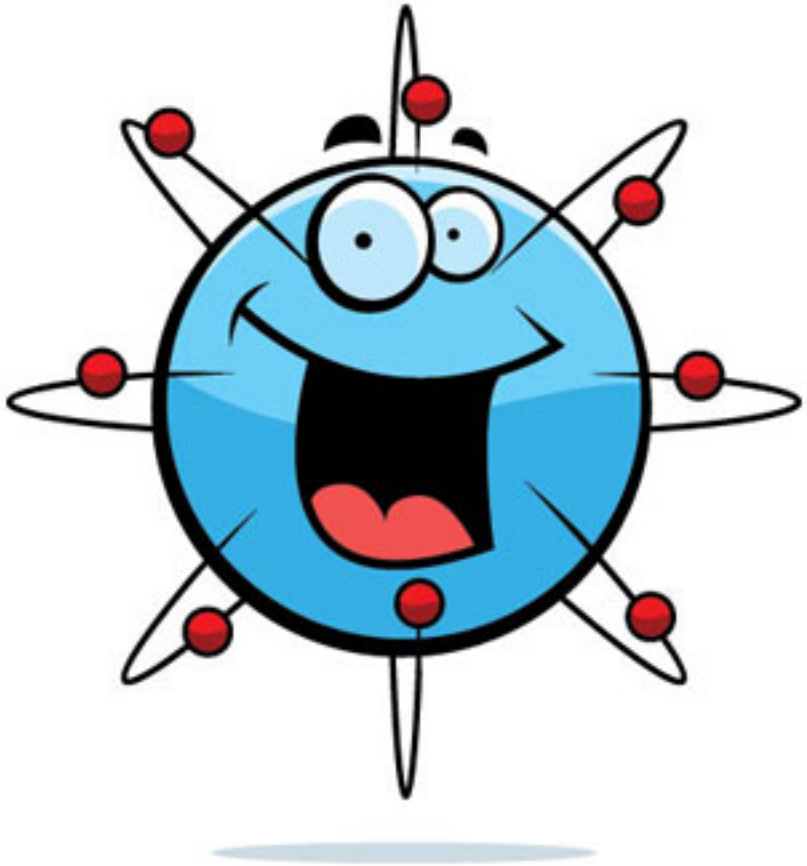
Bunch of nuclei and electrons:
Use Quantum Mechanics!

$$H\Psi = E\Psi$$

$$H = \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_i^2 - \sum_{k}^{N_n}\frac{Z_k e^2}{|\mathbf{r}_i - \mathbf{R}_k|}\right) + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}{}' \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$
$$+ \sum_{k=1}^{N_n} -\frac{\hbar^2}{2m}\nabla_k^2 + \frac{1}{2}\sum_{k=1}^{N_n}\sum_{m=1}^{N_n}{}' \frac{Z_k Z_m e^2}{|\mathbf{R}_k - \mathbf{R}_m|}$$

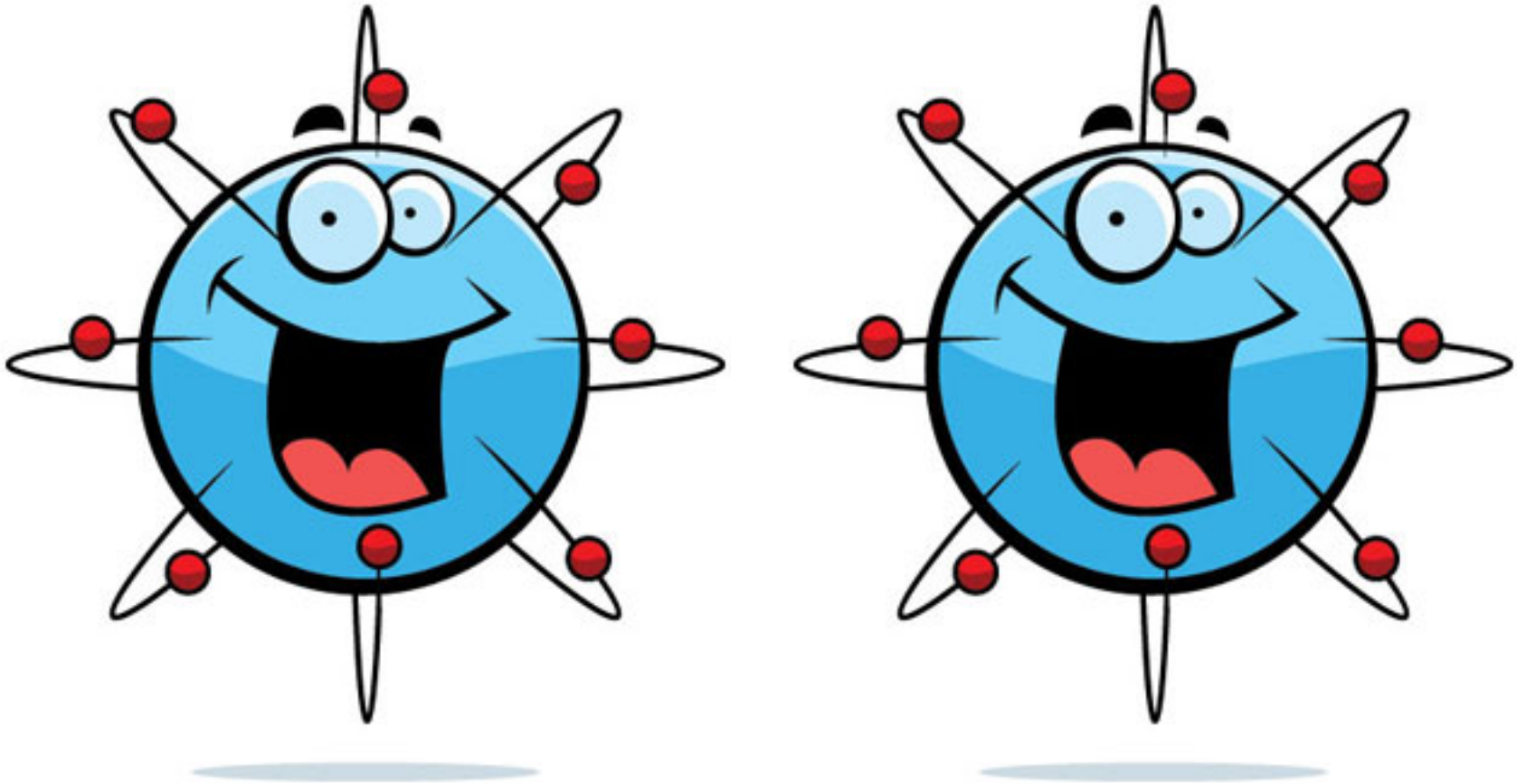
$$\Psi = \Psi(\mathbf{r}_1, ..., \mathbf{r}_N, \mathbf{R}_1, ..., \mathbf{R}_{N_n})$$

Many-body problem

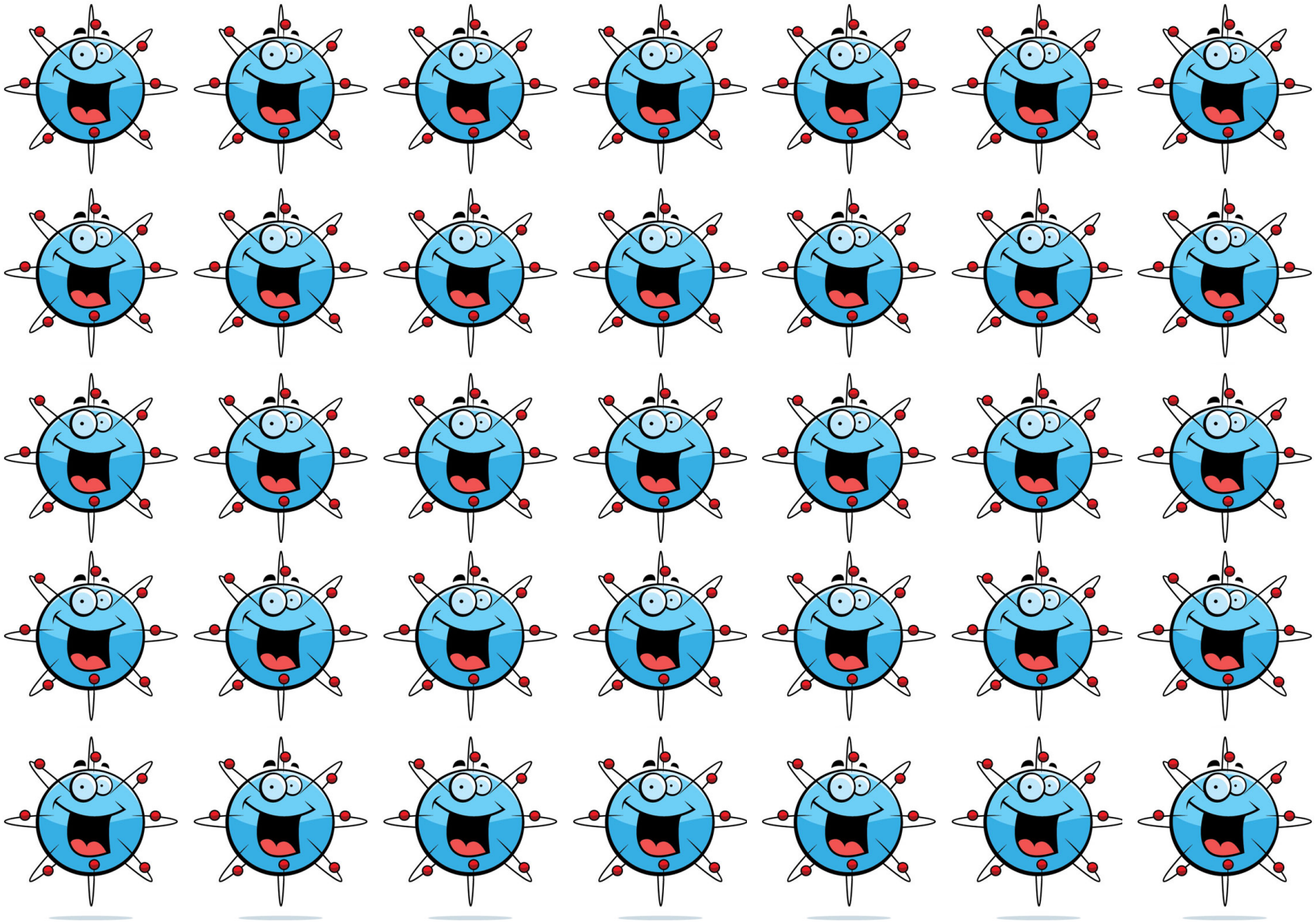


May be solvable

Many-body problem



Many-body problem



Many-body problem: too complicated to solve!

MAX DRIVING THE EXASCALE TRANSITION

P. A. M. Dirac, Proc. Camb. Phil. Soc. **26**, 376 (1930)

Quantum Mechanics of Many-Electron Systems.

By P. A. M. Dirac, St. John's College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received March 12, 1929.)

§ 1. *Introduction.*

The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

Step 1: Born-Oppenheimer approximation

Adiabatic approximation: nuclei are heavy and move much slower than the electrons, so the electronic cloud has sufficient time to relax to its ground state in any instantaneous configuration of the nuclei.

Electronic Schrödinger Equation: $H\Psi = E\Psi$

$$H = \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_i^2 - \sum_{k}^{N_n}\frac{Z_k e^2}{|\mathbf{r}_i - \mathbf{R}_k^0|}\right) + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}{}'\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$+ \sum_{k=1}^{N_n} -\frac{\hbar^2}{2m}\nabla_k^2 + \frac{1}{2}\sum_{k=1}^{N_n}\sum_{m=1}^{N_n}{}'\frac{Z_k Z_m e^2}{|\mathbf{R}_k - \mathbf{R}_m|}$$

$$\Psi = \Psi(\mathbf{r}_1, ..., \mathbf{r}_N, \mathbf{R}_1^0, ..., \mathbf{R}_{N_n}^0)$$

How much storage do we need?

Let‘s see how much disc space we need to store a wavefunction.

Take an atom, e.g. N with 7 electrons; store 10 values per coordinate

How much is $2x10^6$ t?






Born-Oppenheimer

Electronic Schrödinger Equation: $H\Psi = E\Psi$

$$H = \sum_{i=1}^{N} \underbrace{\left(-\frac{\hbar^2}{2m}\nabla_i^2 - \sum_{k}^{N_n} \frac{Z_k e^2}{|\mathbf{r}_i - \mathbf{R}_k^0|} \right)}_{h(\mathbf{r}_i)} + \cancel{\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}{}' \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}} + \cancel{\sum_{k=1}^{N} -\frac{\hbar^2}{2m}\nabla_k^2 + \frac{1}{2}\sum_{k=1}^{N_n}\sum_{m=1}^{N_n}{}' \frac{Z_k Z_m e^2}{|\mathbf{R}_k - \mathbf{R}_m|}}$$

assume independent electrons

$$\longrightarrow H = \sum_{i=1}^{N} h(\mathbf{r}_i)$$

Independent electrons

$$H = \sum_{i=1}^{N} h(\mathbf{r}_i)$$

$$\Psi(\mathbf{r}_1\sigma_1, ..., \mathbf{r}_N\sigma_N) = \frac{1}{\sqrt{N!}} det[\psi_1(\mathbf{r}_1\sigma_1)\psi_1(\mathbf{r}_2\sigma_2)...\psi_N(\mathbf{r}_N\sigma_N)]$$

Slater determinant

$$E = \langle\Psi|H|\Psi\rangle = \sum_{i=1}^{N} \epsilon_i = \sum_{i=1}^{N} \langle\psi_i|h(\mathbf{r}_i)|\psi_i\rangle$$

To calculate an observable we only need single particle orbitals!

Back to N-atom

Let‘s see how much disc space we now need to store a wavefunction.

N with 7 electrons; store 10 values per coordinate

- 7 electrons → **maximally 7 orbitals** $\psi_1, ..., \psi_7$
- Each orbital depends on 3 variables → $\psi_j = \psi_j(x, y, z)$
- 10 entries per coordinate → **10^3 entries**
- in total, for all orbitals → **7×10^3 entries**

→ **7 kB of data**

The coordinates of an electron are independent of the coordinates of all other electrons, because the particles do not interact!

In reality, however, the electrons do interact, so…

Mean-field theories

Maybe we could find a way to map the interacting Hamiltonian

$$H = \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m} \nabla_i^2 - \sum_{k}^{N_n} \frac{Z_k e^2}{|\mathbf{r}_i - \mathbf{R}_k|} \right) + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

onto a non-interacting one, with an effective potential which includes the interaction?

$$H = \sum_{i=1}^{N} h_{eff}(i) = \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m} \nabla_i^2 + V_{eff}(i) \right)$$

Mean field approximations:

- **Hartree-Fock**
- **Density Functional Theory (DFT)**

Hartree equations

D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 89, 111 (1928)

Dr Hartree, The wave mechanics of an atom, etc. 89

The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part I. Theory and Methods. By D. R. HARTREE, Ph.D., St John's College.

[*Received* 19 November, *read* 21 November, 1927.]

Division of electrons into "core" and valence

The potential consists of the "external" potential due to the ions and an approximation to the true electronic one: each electron sees the others as a smooth distribution of negative charge with charge density ρ

$$\rho(\mathbf{r}) = -e \sum |\psi_i(\mathbf{r})|^2$$

$$U_{el}(\mathbf{r}) = e^2 \sum_j \int d\mathbf{r}' |\psi_j(\mathbf{r}')|^2 \frac{1}{|\mathbf{r}_i - \mathbf{r}'|} \qquad U_{ext}(\mathbf{r}) = -Ze^2 \sum_{\mathbf{R}} \frac{1}{|\mathbf{r}_i - \mathbf{R}|}$$

Hartree equations

D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 89, 111 (1928)

Dr Hartree, The wave mechanics of an atom, etc. 89

The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part I. Theory and Methods. By D. R. HARTREE, Ph.D., St John's College.

[*Received* 19 November, *read* 21 November, 1927.]

Hartree equations (one for each occupied one-electron level):

$$-\frac{\hbar^2}{2m}\nabla_i^2\psi_i(\mathbf{r}) + U_{ext}(\mathbf{r})\psi_i(\mathbf{r}) + \sum_j \int d\mathbf{r}'|\psi_j(\mathbf{r}')|^2 \frac{e^2}{|\mathbf{r}_i - \mathbf{r}'|}\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

Solved **self-consistently**: for a trial electronic potential determine the one-electron wavefunctions then use them to construct the new potential and iterate further.

Even though approximate, already quite complex and difficult to solve!

Hartree-Fock equations

V. Fock, Z. Physik **61**, 126 (1930)

J. C. Slater, Phys. Rev. **35**, 210 (1930)

Hartree equations can be derived from the trial function:

$\Psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, ..., \mathbf{r}_N s_N) = \psi_1(\mathbf{r}_1 s_1)\psi_2(\mathbf{r}_2 s_2)...\psi_N(\mathbf{r}_N s_N)$, which is not antisymmetric, as required by the Pauli principle. By using a Slater determinant instead, one arrives to Hartree-Fock equations that also contain an exchange term:

$$-\frac{\hbar^2}{2m}\nabla_i^2\psi_i(\mathbf{r}) + U_{ext}(\mathbf{r})\psi_i(\mathbf{r}) + U_{el}(\mathbf{r})\psi_i(\mathbf{r})$$
$$-\sum_j \int d\mathbf{r}' \frac{e^2}{|\mathbf{r}_i - \mathbf{r}'|}\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')\psi_j(\mathbf{r})\delta_{s_i s_j} = \varepsilon_i\psi_i(\mathbf{r})$$

Hartree-Fock & Density Functional Theory (DFT)

Wave-function based

- $\Psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, ..., \mathbf{r}_N s_N)$
- Optimize $E = \dfrac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$

Many complicated wave functions.

Can we try to extract information about physical systems with an integrated quantity instead?

Hartree-Fock & Density Functional Theory (DFT)

Wave-function based

- $\Psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, ..., \mathbf{r}_N s_N)$
- Optimize $E = \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$

Density based

- Use $n(\mathbf{r}) = N \sum_{s_1} ... \sum_{s_N} \int d\mathbf{r}_2 ... \int d\mathbf{r}_N \Psi^*(\mathbf{r} s_1, \mathbf{r}_2 s_2, ..., \mathbf{r}_N s_N) \Psi(\mathbf{r} s_1, \mathbf{r}_2 s_2, ..., \mathbf{r}_N s_N)$
- Minimize functional $E[n(\mathbf{r})]$, provided that it exists and is (to some extent) known

The Essence of DFT

P. Hohenberg, W. Kohn, *Phys. Rev.* 136, B864 (1964)

Theorem 1: *For a given external potential V, the ground-state properties of a system are uniquely determined by the electron density alone, i.e. they are functionals of the density.*

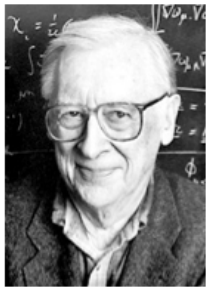
Theorem 2: *The exact ground-state density minimizes the energy functional E[n(**r**)]*

The Nobel Prize in Chemistry 1998
Walter Kohn, John Pople

The Nobel Prize in Chemistry 1998

Walter Kohn

Prize share: 1/2



John A. Pople

Prize share: 1/2

The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn *"for his development of the density-functional theory"* and John A. Pople *"for his development of computational methods in quantum chemistry"*.

Kohn-Sham Equations

W. Kohn, L. J. Sham, *Phys. Rev.* **140**, A1133 (1965)

How do we now use DFT to calculate materials' properties?

- Start from a **non-interacting electron gas** in a potential v_s → one-electron Schrödinger equation:

$$\left(-\frac{\nabla^2}{2} + v_s\right)\varphi_i = \epsilon_i \varphi_i$$

- For *N* electron states, construct the *one-particle electron density* from the lowest-lying *one-particle states:*

$$n_{op}(\mathbf{r}) = \sum_{i=1}^{N/2} 2 \mid \varphi_i(\mathbf{r}) \mid^2$$

- For small variations around the ground-state density E is stationary:

$$0 = \delta E_{op} = E_{op}[n_{op}(\mathbf{r}) + \delta n_{op}(\mathbf{r})] - E_{op}[n_{op}(\mathbf{r})]$$

$$0 = \delta T_{op}[n_{op}] + \int \delta n(\mathbf{r}) v_s(\mathbf{r})\, d\mathbf{r}$$ yields the exact ground state density corresponding to v_s

Kohn-Sham Equations

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Now to an **interacting system**:

Physics professors shouldn't teach geometry.

- Now assume that we can find ***an effective potential*** v_s so that $n($
where $n(\mathbf{r})$ is the ***ground state density of an interacting system.***

$$E[n(\mathbf{r})] = T_{op}[n(\mathbf{r})] + \int n(\mathbf{r}) v_{ext}(\mathbf{r})\, d\mathbf{r} + \frac{e^2}{2} \int\int \frac{n(\mathbf{r}) \cdot n(\mathbf{r}')}{|\,\mathbf{r} - \mathbf{r}'\,|}\, d\mathbf{r}\, d\mathbf{r}' + E_{xc}[n(\mathbf{r})]$$

kinetic energy of the non-interacting system

Hartree term

Exchange and correlation; contains the exchange interactions and the corrections to the kinetic energy

Approximate!

- From $0 = \delta T_{op}[n] + \int d\mathbf{r}\, \delta n(\mathbf{r}) \left[v_{ext}(\mathbf{r}) + \int e^2 \frac{n(\mathbf{r}')}{|\,\mathbf{r} - \mathbf{r}'\,|}\, d\mathbf{r}' + \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \right]$

$$\rightarrow\ v_s(\mathbf{r}) = v_{ext}(\mathbf{r}) + \int e^2 \frac{n(\mathbf{r}')}{|\,\mathbf{r} - \mathbf{r}'\,|}\, d\mathbf{r}' + \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

$$\rightarrow\ \left(-\frac{\nabla^2}{2} + v_s \right) \varphi_i = \epsilon_i \varphi_i$$ *Equations solved self-consistently*: guess $v_s \rightarrow \varphi_i \rightarrow n$

Local Density Approximation (LDA)

W. Kohn, L. J. Sham, *Phys. Rev.* **140**, A1133 (1965)

- Kohn-Sham equations transfer the problem of ***finding the correct density*** to ***finding the correct exchange-correlation potential***.

- The simplest approximation is LDA, which exploits the nearsightedness of the electronic matter:

$$E_{xc}^{LDA}[n(\mathbf{r})] = \int \varepsilon_{xc}^{hom}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r}$$

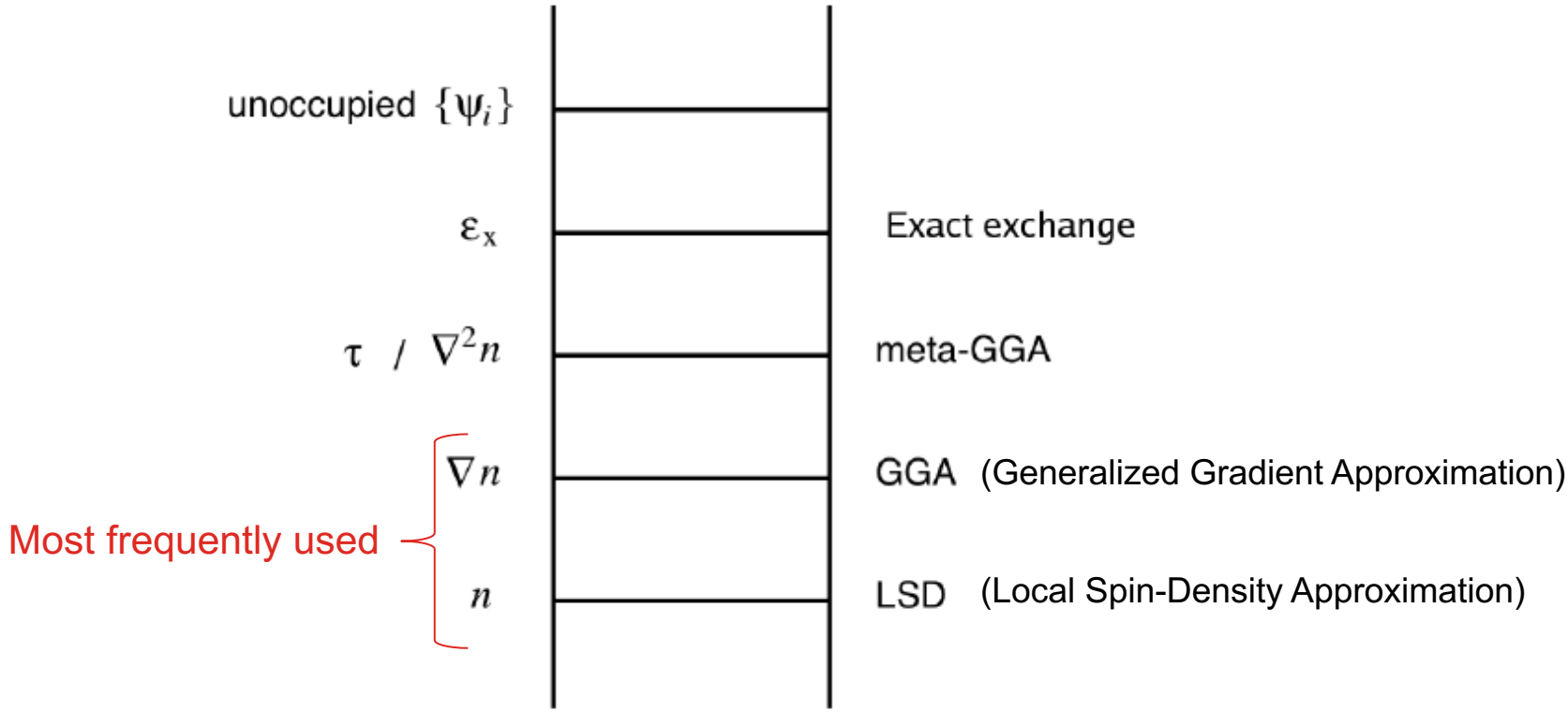
where $\varepsilon_{xc}^{hom}(n)$ is exchange and correlation energy per particle of a ***homogeneous*** electron gas (HEG).

Kohn & Sham: ***"We do not expect an accurate description of chemical binding"***

“Jacob’s ladder” of approximations

(according to J. P. Perdew)

Improve LSD by incorporating exact constraints successively



“And he dreamed, and behold a ladder set up on the earth, and the top of it reached to heaven: and behold the angels of God ascending and descending on it.” Genesis 28:12 (King James Version).

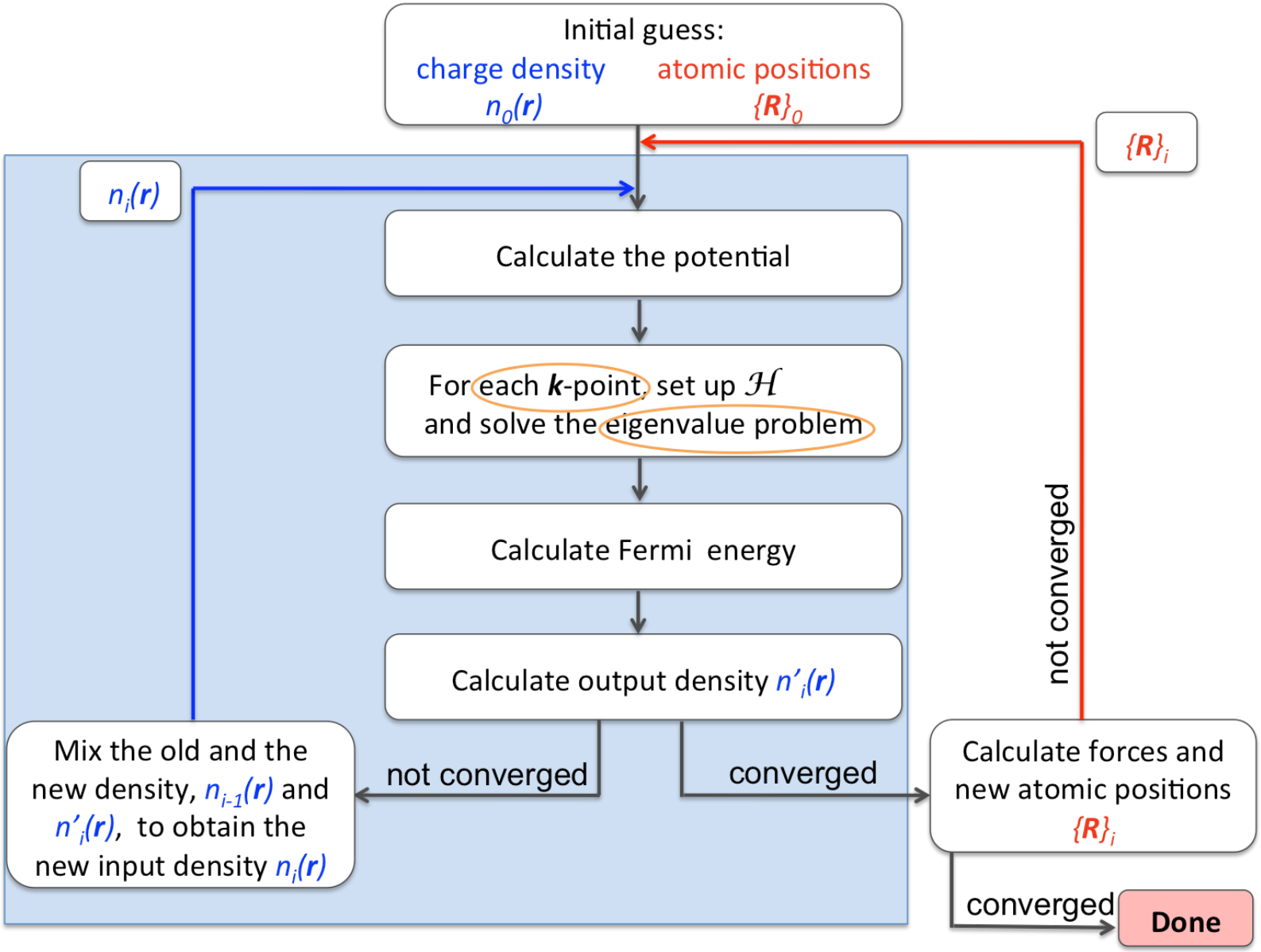
More on Thursday: lecture by Matthias Redies!

Kohn-Sham: cautionary notes

- Kohn-Sham orbitals have, strictly speaking, **no** physical meaning, except that $n(\vec{r}) = \sum_{i=1}^{N} |\varphi_i(\vec{r})|^2$ is the exact density of the interacting system. In particular, $det(\varphi_i(\vec{r}))$ is not to be taken as an approximation to the many-body wave-function of the system.

- Likewise, the orbital energies ϵ_i have in general **no** physical meaning,

Self consistency cycle and structure optimisation



How to tell the computer what to do?

$$\left(-\frac{\nabla^2}{2} + v_s\right)\varphi_i = \epsilon_i \varphi_i$$

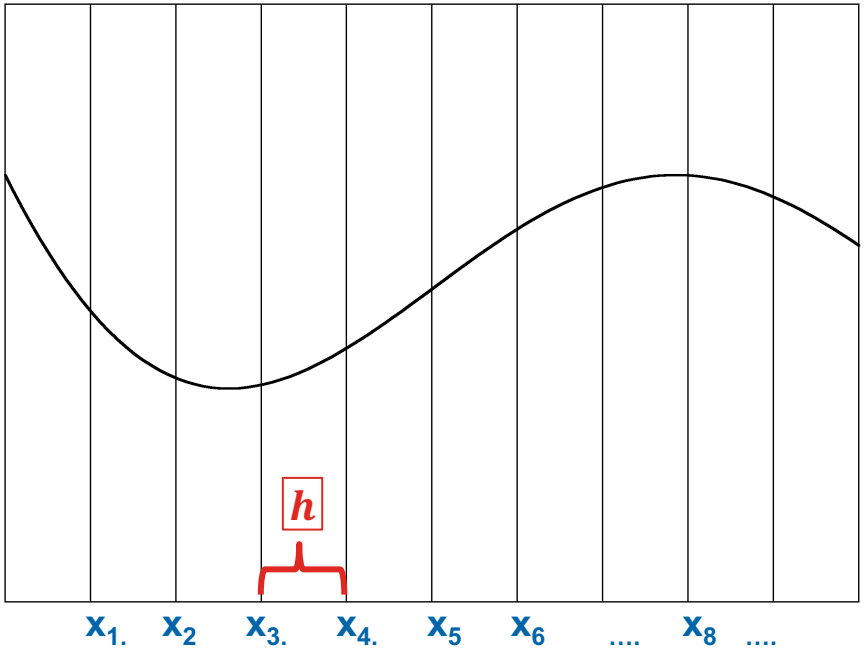
How to tell the computer what to do?

Turn Kohn-Sham equations into matrix equations!

Two options:

- Discrete real space grid
- Expansion in a basis set

Discrete grids: 1D illustration



$f(x)$

$$f(x) \rightarrow \begin{pmatrix} f(x_1) \\ f(x_1) \\ f(x_1) \\ \vdots \\ f(x_n) \end{pmatrix}$$

Derivatives → finite differences:

Simplest formula for the second derivative is:

$$\left.\frac{d^2 f}{dx^2}\right|_{x_j} = \frac{f(x_{j+1}) - 2f(x_j) + f(x_{j-1})}{h^2}$$

A 1D Kohn-Sham equation takes the form:

Boundary conditions!

$$\begin{pmatrix} -\frac{1}{2h^2} & v_s(x_1) + \frac{1}{2h^2} & -\frac{1}{2h^2} & & & \\ & -\frac{1}{2h^2} & v_s(x_2) + \frac{1}{2h^2} & -\frac{1}{2h^2} & & \\ & & -\frac{1}{2h^2} & v_s(x_2) + \frac{1}{2h^2} & -\frac{1}{2h^2} & \\ & & & \ddots & \ddots & \ddots \\ & & & & -\frac{1}{2h^2} & v_s(x_n) + \frac{1}{2h^2} & -\frac{1}{2h^2} \end{pmatrix} \begin{pmatrix} \varphi_k(x_0) \\ \varphi_k(x_1) \\ \varphi_k(x_2) \\ \vdots \\ \varphi_k(x_{n+1}) \end{pmatrix} = \epsilon_k \begin{pmatrix} \varphi_k(x_0) \\ \varphi_k(x_1) \\ \varphi_k(x_2) \\ \vdots \\ \varphi_k(x_{n+1}) \end{pmatrix}$$

Discrete grids: 1D illustration

Boundary conditions:

- For finite systems K-S orbitals are zero on the boundary
- For periodic systems: $\boldsymbol{\varphi_k(x_0)= \varphi_k(x_n)}$, $\boldsymbol{\varphi_k(x_1)= \varphi_k(x_{n+1})}$

Integrals are calculated as finite sums:

$$\int_{x_1}^{x_n} dx\, f(x) = h \sum_{j=1}^{n} f(x_j)$$

Of course, one introduces an **error by discretizing the functions, which depends on the spacing of the grid points.**

Expansion into basis functions

Choose some functions $\phi_\mu(\vec{r})$ and expand the wavefunction:

$$\varphi(\vec{r}) = \sum_{\mu}^{N_b} c_\mu \phi_\mu(\vec{r})$$

→ The differential equation turns into a linear algebra equation

$$\sum_{\nu} H_{\mu\nu} c_{i\nu} = \epsilon_i \sum_{\nu} S_{\mu\nu} c_{i\nu}$$

In short:

$$Hc_i = \epsilon_i S c_i$$

Two matrices

- Hamiltonian contains the matrix elements of the kinetic energy and of the potential:

$$H_{\nu\mu} = \int_V d^3r \phi_\nu^*(\vec{r}) \left(-\frac{1}{2}\nabla^2 + v_s(\vec{r}) \right) \phi_\mu(\vec{r})$$
$$= T_{\nu\mu} + V_{\nu\mu}$$

- The Overlap matrix:

$$S_{\nu\mu} = \int_V d^3r \phi_\nu^*(\vec{r}) \phi_\mu(\vec{r})$$

- Overlap is diagonal for orthogonal basis functions

The choice of the basis functions

The choice of the basis depends on two criteria:

1) **Boundary conditions**

- For finite systems $\phi_i(\vec{r}) \xrightarrow{r \to \infty} 0$
- For periodic systems: plane waves

2) **Generality vs. suitability to the specific problem**

- The closer the basis functions are to the actual K-S orbitals, the fewer basis functions one needs:

If we manage to guess a basis function that equals the wavefunction, a single expansion coefficient would be enough

$$\varphi(\vec{r}) = \sum_{i}^{1} c_i \phi_{i=1}(\vec{r})$$

- One cannot, however, chose a different basis set for each problem!

Examples: Local basis sets

Construct basis functions that are centered at the atoms

- Gaussian basis functions

Atomic position

$$\phi(\vec{r}) = \frac{1}{N} e^{-\alpha(\vec{r}-\vec{R})^2}$$

(usually linear combinations of such Gaussians are used).

- Slater type

  These functions decay exponentially for large distance and have the correct behavior close to the nuclei

$$\phi(r) = \frac{1}{N} |(r - R)|^{n-1} e^{-\eta(r-R)}$$

(n is an integer -> principle quantum number)

These functions also need an angular part →usually spherical harmonics

Examples: Plane waves (for periodic systems)

$$\phi_{\vec{g}}(\vec{r}) = \frac{1}{N} e^{i\vec{g}\vec{r}}$$

Advantages:

- Orthonormal basis set
- Single convergence parameter: number of plane waves
- Plane waves are momentum eigenfunctions → the kinetic energy is diagonal

$$T_{\vec{g},\vec{g}'} = \frac{1}{2}|\vec{g}|^2 \delta(\vec{g} - \vec{g}')$$

- Plane waves easily fulfill the Bloch ansatz for periodic systems by taking

$$\vec{g} = \vec{k} + \vec{G}$$

Examples: Plane waves (for periodic systems)

$$\phi_{\vec{g}}(\vec{r}) = \frac{1}{N} e^{i\vec{g}\vec{r}}$$

Advantages:

- Potential matrix elements are given by the Fourier transform of the potential

$$\begin{aligned} V_{\vec{g},\vec{g}'} &= \frac{1}{N^2} \int_V d^3 r V(r) e^{i(\vec{g}'-\vec{g})\vec{r}} \\ &= V_{FT}(\vec{G}' - \vec{G}) \end{aligned}$$

The non-trivial part of the story…

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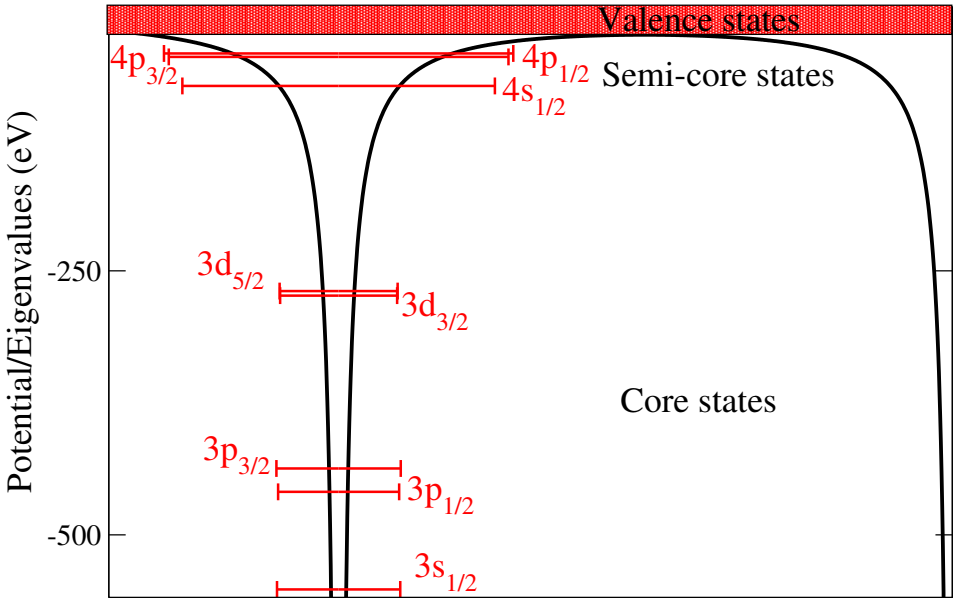
Two problems:

- The ionic potentials have an integrable pole at the position of the ions

→ Gaussian and Slater type orbitals we can solve the integral analytically, but for grids and plane waves we have a problem (infinitely many grid points / plane-waves needed to describe the pole)

- Core electrons are usually localized near the ion

→ Localized functions need finer grids / many plane waves, while at the same time core electrons are not essential for binding and general electronic behavior.



The non-trivial part of the story…

MAX DRIVING THE EXASCALE TRANSITION

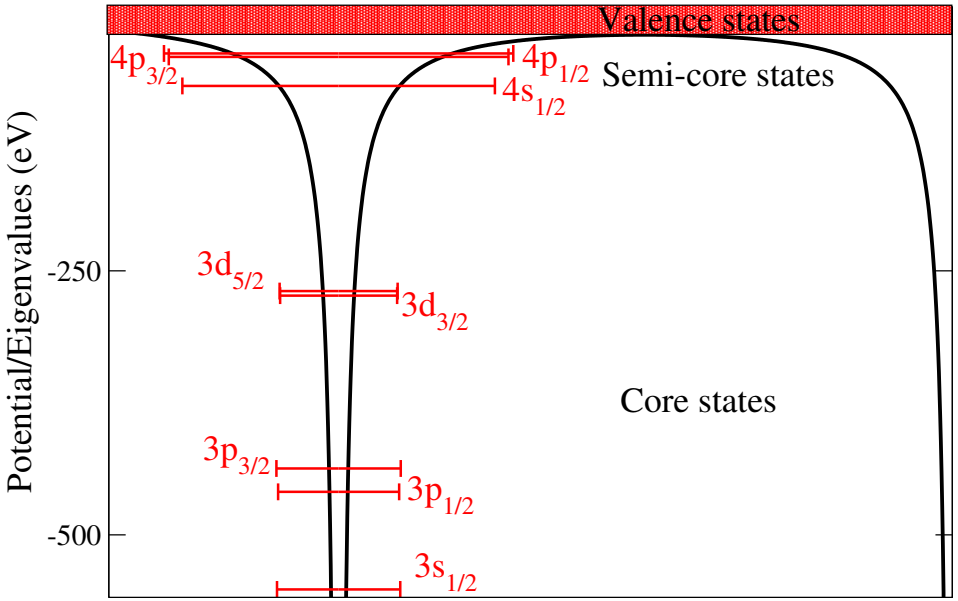
Two possibilities:

- Pseudopotentials

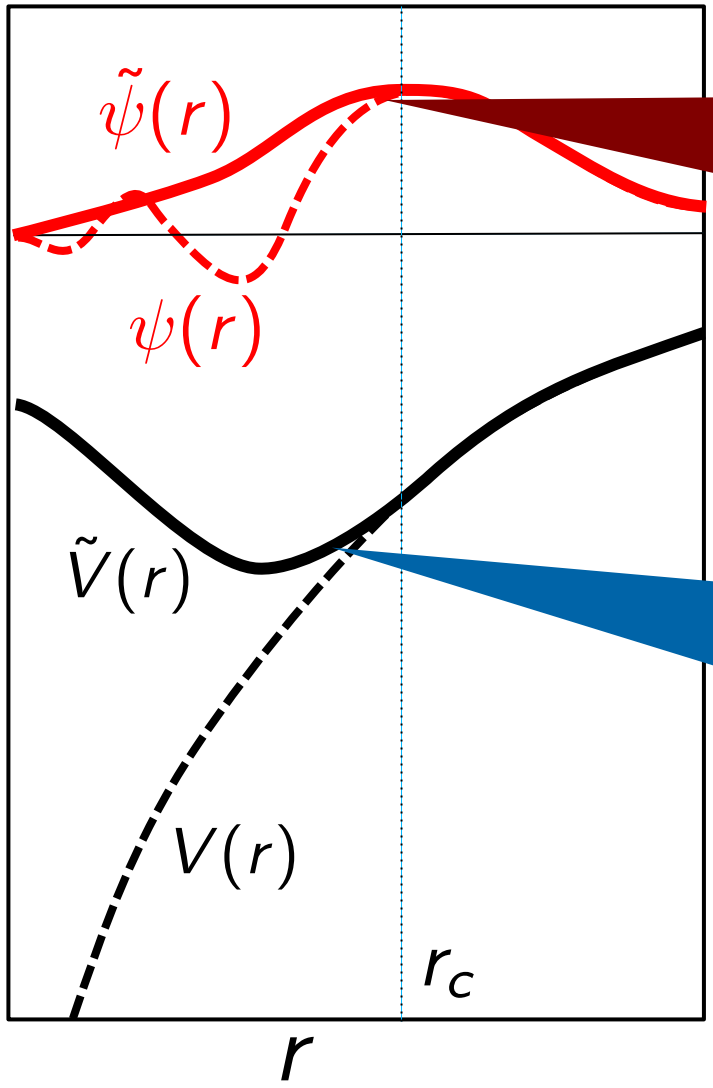
→ Modify the potential to make it easier to treat

- Augmented plane waves

→ Treat core and valence electrons differently → Gregor Michalicek's lecture



Idea behind a pseudo-potential



Replace AE wavefunction by pseudo-wavefunction

→ smooth nodeless wavefunction

→ same as AE outside some radius

→ inside the core radius the nodeless wavefunction is meaningless

Remove the 1/r singularity

→ "remove" core states

→ remove numerical difficulties

Create a smooth potential

Idea behind the augmented plane waves

Partition space:

- **MT spheres**

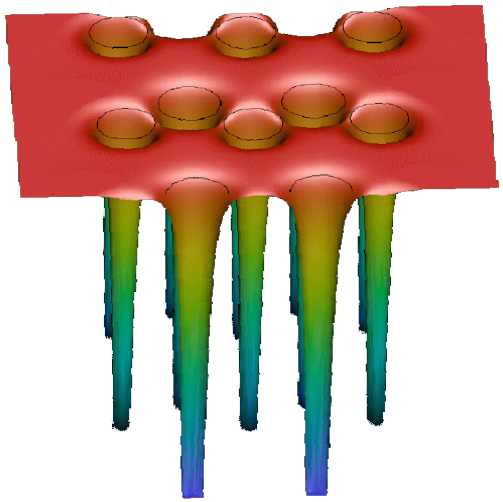
Potential is spherically symmetric

→ use the solutions of the radial part of the Schrödinger equation

- **Interstitial**

Potential is small

→use plane waves



Stay tuned for more: lecture by Gregor Michalicek!

Take-home messages

- Many-body problems: difficult to solve, large memory needed for storing the wave function; approximations are needed
- Mean-field approaches: Hartree-Fock & DFT
- DFT: given an external potential, the ground-state density uniquely determines the ground-state properties and minimizes the energy functional.
- Kohn-Sham equations map a system of interacting particles onto a system of non-interacting particles with the same density.
- Approximations to the exchange-correlation functional are necessary
- One seeks a self-consistent solution to the K-S equations
- Various computational methods exist, the right choice depending on several factors, such as e.g. the type of the system to be treated and whether one is interested in the core electrons or not

Thank you for your attention!